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Can volcanic gases be used to reconstruct paleo-environments?

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How water can be used as a paleo-indicator

When volcanoes erupt, they release gas into the environment. If a volcano erupts under an ice sheet or glacier, the amount of gas that can escape is reduced. Dixon *et al.* (2002) argues that the amount of gas released is dependent on the thickness of ice because volatile exsolution is a function of the pressure experienced by the magma.

Because the primary volatile in most magmas is water, it is therefore possible to reconstruct the thickness of ice above a volcano, when it erupted by analysing the amount of water retained in volcanic glass.

CO_2 and other influences

A major problem with the simple ice thickness model is that other factors, apart from pressure, affect the solubility of water. These include the CO_2 content and the eruptive temperature (Newman & Lowenstern, 2002). As figure 2 illustrates, if a rock has a water content of 1 wt %, this could mean that either: (i) the ice thickness above the volcano was 950 m it the lava was erupted at 850ºc with a CO_2 content of 0 ppm; or (ii) the ice thickness was 1700 m if it was erupted at 950ºC and had a CO_2 content of 30 ppm. These are all within the realms of normal eruptive conditions. The problem is intensified by the fact that the majority of analytical techniques can not detect if there is CO_2 below 30 ppm (Tuffen *et al.,* unpublished). However, if there has been significant H_2O degassing it is likely that the CO_2 content will be 0 ppm (Dixon *et al.,* 2002).

The good news is that the effects of CO_2 and temperature are quite well known, so the model (Newman & Lowenstern, 2002) can be used. The bad news is that there are other influences which have not been considered and are poorly understood. One example is fluorine. This has the potential to significantly influence water solubility (Aiuppa *et al.,* 2008) (figure 3).

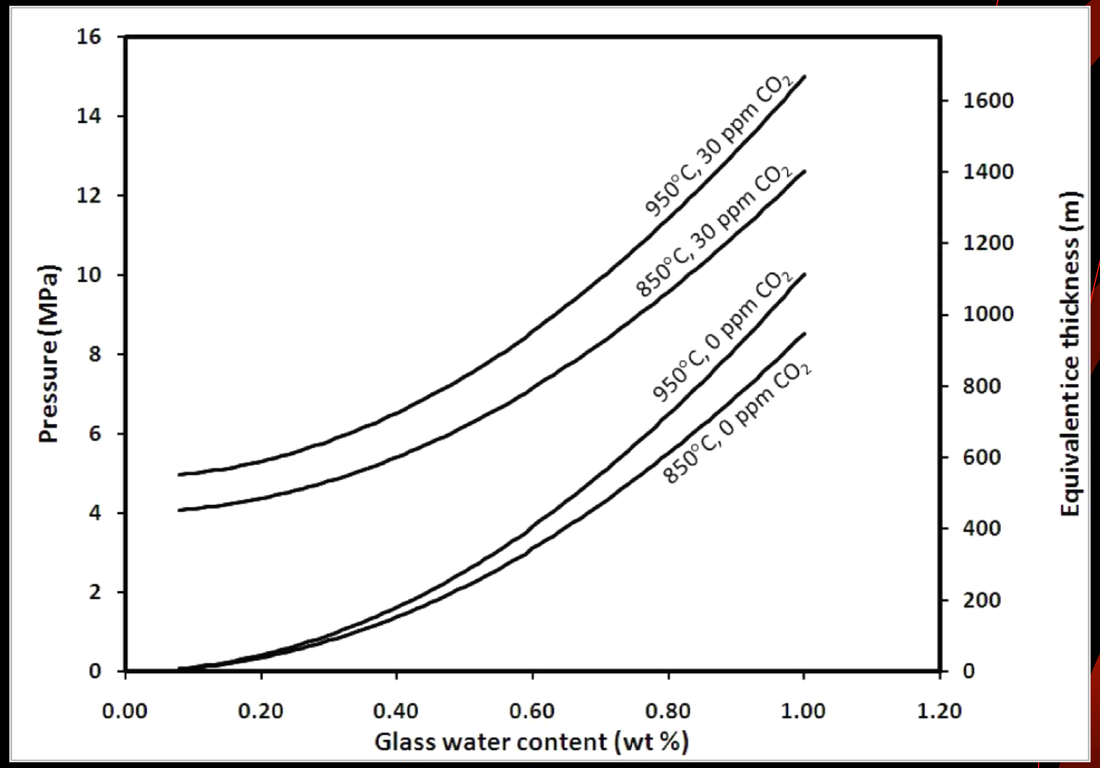

Figure 2: Graphs showing the effects of CO_2 and temperature on water solubility within rhyolititc melts based on calculations made in VolatileCalc (Newman & Lowenstern, 2002).

Why you lose gas as you climb a volcano

As you climb a volcano that was once covered in ice , the amount of volatiles trapped within the rocks decreases (Fig. 1) because less ice covered the top of the volcano than the bottom. The more ice, the higher the confining pressure, making volatile species more soluble in the magma. Thus, there is a negative correlation between water content and altitude (Dixon *et al.,* 2002).

My results

I have used Fourier Transform Infrared spectroscopy to determine the water content of a series of rocks collected from different elevations of a subglacial volcano called Bláhnúkur in southern Iceland. Figure 1 shows these results plotted against theoretical ice thickness curves. My results suggest that when Bláhnúkur erupted, 95 thousand years ago (unpublished data), the ice surface was at 1050 m above sea level in this part of Iceland. This is a very plausible result and corresponds well with the inferred ice thickness at ~60 ka in the same region.

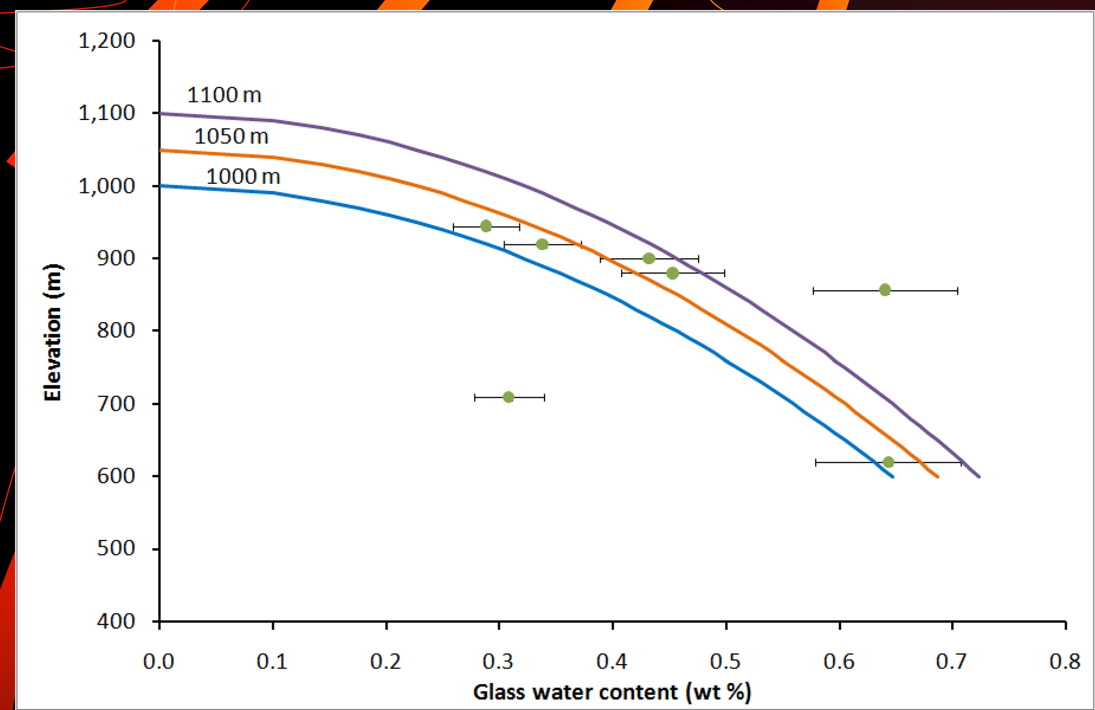

Figure 1: Theoretical ice thickness curves (solid lines) showing the negative correlation between water content and elevation, calculated using VolatileCalc (Newman & Lowenstern, 2002) with the assumption that the lava was erupted at 850ºC and with 0 ppm CO_2. Also plotted is data from my samples from Bláhnúkur (green dots).

How do you know that water hasn't been added at a later date?

It is possible that volcanic rocks can absorb water post eruption, through cracks and fractures (Denton *et al.,* 2009). However, these later additions tend to leave the H_2O in the form of molecular water, whereas water retained within the melt tends to be in the form of hydroxyl ions which are intricately bonded with the other atoms. The percentage in the two different forms can be quite easily determined through spectroscopy (Forbes, 2008) or through thermal analysis (Eichelberger & Westrich, 1981).

F variety questions how representative the data is

In order to get a truly accurate value for the water content at different elevations one must analyse the entire volcano. Since my rucksack wasn't big enough to fit all of these rocks into, one has to rely on a few choice samples. But are these representative? In order to answer this question it is important to understand how much the volatile contents can vary over a small spatial scale and as figure 3 shows, they can vary a lot. Figure 3 shows that the concentration of fluorine can increase by a factor of two, over a distance of ~0.2mm (the difference between the white and dark grey band). Unfortunately, the technique used to determine the water content did not have as good a spatial resolution as that used to determine F (Edmonds, 2008) but the fact that F varies so much and that F can influence water solubility (Aiuppa *et al.,* 2008) , throws up a big warning when interpreting data – is it representative of the water content at that elevation?

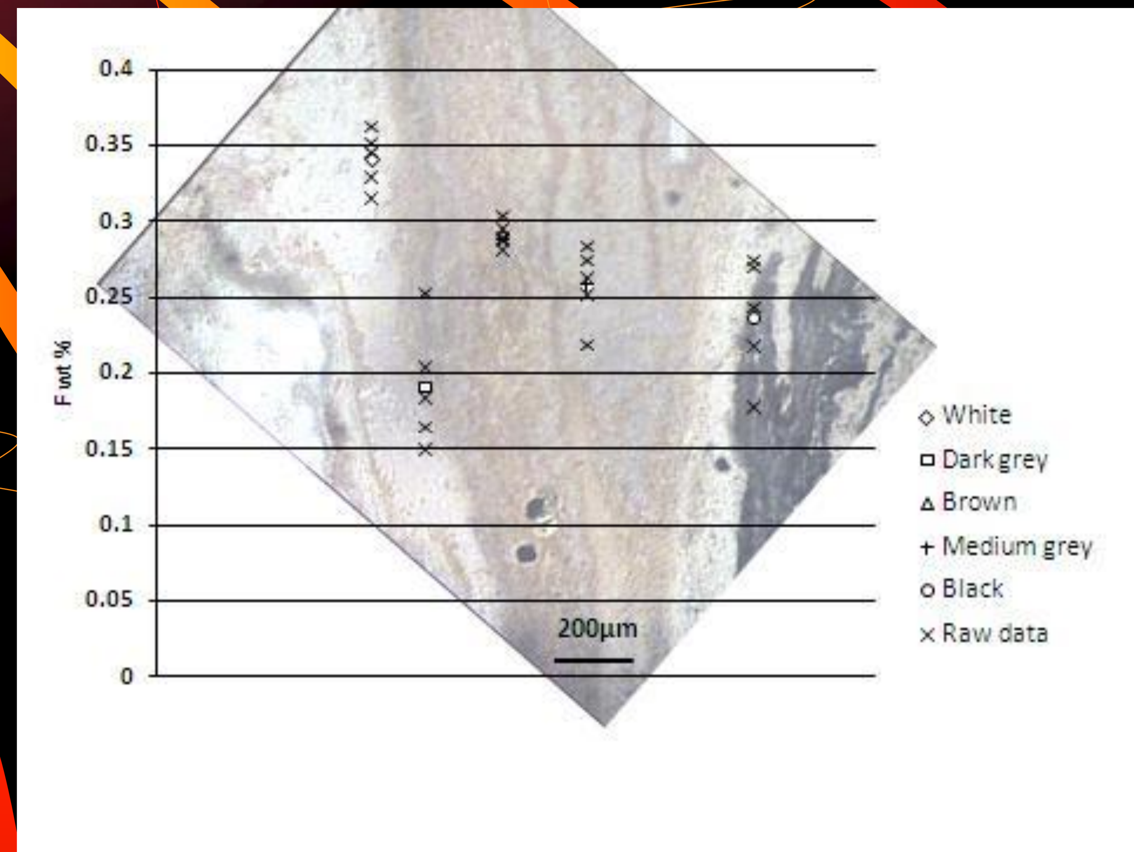

Figure 3: A plot showing fluorine data for different coloured bands within a sample of obsidian taken from Bláhnúkur. The x's show the raw data and the solid shapes show the average values for each band.

Other ways of loosing gas

There are some other explanations of why volatile contents decrease with altitude. For example, the negative correlations between water content and altitude can be explained simply by time. As the eruption progresses, gas is able to escape more freely, meaning that by the end of the eruption, most of the gas can escape and this leaves the top of the volcano depleted in volatiles. Another possible explanation is that the magma was erupted from a zoned magma chamber (Forbes, 2008)

Equilibrium degassing

For the model, to work there needs to be equilibrium degassing, which means that the eruption rate needs to be slow enough to allow this to happen (Tuffen *et al.,* in prep.)

Further work

There are two anomalous results within Figure 1. Are these errors - do they disprove the theory, or is there a scientific explanation? Maybe meltwater was able to drain away, reducing the pressure, or maybe the erupted material never made it to the surface of the volcano and therefore is experiencing loading from both rock and ice and therefore a greater quenching pressure. I am currently analysing more samples to throw light on this issue.

What if there's more than ice above?

The amount of water retained within the rock is dependent on the pressure exerted by the weight of the ice that is bearing down on the volcano (Dixon *et al.,* 2002). There are then a number of assumptions used to convert this pressure into an ice thickness. E.g. In our calculations, we have assumed that the density of ice is 917 kg m^{-3} (Hoskuldsson & Sparks, 1997). However, there may be other things, apart from ice, above the extruding lava. For example, many glaciers and ice sheets have a top surface of snow and firn which has a lower density than ice. On the other hand, the lava could become quenched before it reaches the volcano-ice interface, in which case there will also be rock adding to the pressure felt by the lava. As a final example, the extruding lava may melt a subglacial cavity and potentially produce significant quantities of meltwater altering the density. The meltwater may then drain away creating conditions of ambient pressure, effectively reducing the apparent ice thickness to zero (Tuffen *et al.,* in prep.).

References

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